



Efficient production of propylene in the catalytic conversion of glycerol



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ABSTRACT

Vapor-phase catalytic conversion of glycerol into propylene was performed over Cu/Al₂O₃ and acid-loaded Cu/Al₂O₃ catalysts in an H₂ flow at ambient pressure. Acidic substances such as WO₃, MoO₃, V₂O₅ and H₃PO₄ were loaded on a commercial Cu/Al₂O₃. The addition of WO₃ was found to be effective for promoting the formation of 1-propanol and propylene from glycerol, and 9.3 wt% WO₃-loaded Cu/Al₂O₃ (WO₃/Cu/Al₂O₃) catalyst showed the best catalytic performance. WO₃/Cu/Al₂O₃ calcined at a low temperature of 320 °C had the largest number of acid sites and gave a 1-propanol selectivity of 38.2% and a propylene selectivity of 47.4% in an H₂ flow at 250 °C. The catalytic reaction of glycerol was performed over double-bed catalysts, in which WO₃/Cu/Al₂O₃ was charged in the upper bed and a commercial silica–alumina was charged in the lower bed, to promote the conversion of 1-propanol into propylene. A high propylene selectivity of 84.8% was obtained over the double-bed catalysts at 100% glycerol conversion. An efficient catalytic process for the production of propylene from glycerol was proposed.

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1. Introduction

In recent years, there is an increasing interest on the use of biodiesel as an alternative fuel [1,2]. The production of biodiesel is 22.7 million metric tons in 2012, and is forecasted increasing to 36.9 million metric tons in 2020 [2]. The rapid increase in biodiesel production has led to an oversupply of crude glycerol, and the effective utilization of glycerol has attracted much attention in the past decade [1,2]. Numerous efforts have been reported on the conversion of glycerol into value-added products, such as acrolein [1–6], acrylic acid [7–10], lactic acid [11,12], glycidol [13,14], hydroxyacetone (HA) [15–17], 1,2-propanediol (1,2-PDO) [18–38], 1,3-propanediol [36–42], and 1-propanol (1-PO) [43,44].

Hydrogenolysis of glycerol into 1,2-PDO, which is a valuable chemical mainly used for producing polymers, has been intensively reported over various metal catalysts such as Cu [18–26], Rh [27,28], Ru [29,30], Ni [31,32], Pt [33,34], and Ag [26,35]. In this reaction, HA is primarily generated in the dehydration of glycerol, and then hydrogenated into 1,2-PDO [15,16]. In our latest paper, a high 1,2-PDO yield of 98.3% was obtained over Ag-modified Cu/Al₂O₃

catalyst in vapor phase at a gradient temperature from 170 to 105 °C under ambient hydrogen pressure flow conditions [26].

Because of the availability of 1,2-PDO from glycerol, several research groups investigated the conversion of 1,2-PDO to form 1-PO [43–45] and propanal (PA) [46–49]. In the hydrogenolysis of 1,2-PDO using iridium complex catalyst, Foskey et al. reported that the presence of water in the reaction mixture gave improved selectivity to 1-PO, and that a 95% yield of 1-PO was achieved at 125 °C and 0.7 MPa [45]. Amada et al. also reported that the selectivity to 1-PO reached 74% with a conversion of 86.6% at 120 °C and 8 MPa together with the competitive formation of 2-propanol in the hydrogenolysis of 1,2-PDO in a liquid phase using Rh–ReOx/SiO₂ catalyst [43]. They also performed a reaction using glycerol as the reactant, and a 76% yield of 1-PO was obtained over Rh–ReOx/SiO₂ at 120 °C and 8 MPa. We have recently developed a new type of solid acid catalyst such as silica-supported WO₃ for the 1,2-PDO dehydration into PA [49]. The silica-supported WO₃ catalyst calcined at 320 °C had a large number of acid sites, and 93.5% selectivity to PA was achieved with a complete conversion at a reaction temperature of 250 °C.

The production of propylene which is an important starting chemical in the petrochemical industry, from renewable resources has also attracted much attention in recent years. Glycerol is an abundant renewable resource for C3 chemicals, and it is beneficial that propylene is produced from glycerol via the further dehydration of 1-PO derived from glycerol via 1,2-PDO and PA. In the

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Table 1
Hydrogenolysis of glycerol over Cu/Al₂O₃, T317 and N242.^a

Catalyst	Temp. (°C)	Conv. ^b (%)	Selectivity (%) ^b										
			Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
T317	190	98.3	0.5	0	2.5	0	32.1	54.3	0	0.2	0	0	0.2
	220	100	1.5	0	1.7	0.1	25.6	35.5	0	6.2	12.1	0.5	18.3
	250	100	4.1	2	0.7	3.2	10.7	6.1	1.7	22.6	27.8	1	50.4
N242	190	79.5	0	0	2.9	0	42.6	51.2	0	0	0	0	0
	220	99.2	2.1	0.1	4.5	0	37.6	46.9	0	0.1	0	0	0.1
	250	100	5.2	0.9	8.1	0.9	41	30.8	0	1.3	0	0	1.3

^a Reaction conditions: catalyst weight, 1 g; H₂ flow rate, 60 cm³ min⁻¹; feed rate of glycerol solution, 1.32 cm³ h⁻¹. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h. (EG, ethylene glycol; HA, hydroxyacetone; 1,2-PDO, 1,2-propanediol; PA, propanal; 1-PO, 1-propanol.)

latest report, propylene has been produced with a selectivity of 85% in the 100% conversion of glycerol in a flow reactor loaded double-bed catalysts of Ir/ZrO₂ and HZSM-5 at 250 °C and 1 MPa, in which 1-PO was an intermediate of propylene [50]. In this study, the catalytic conversion of glycerol into propylene was investigated over acid-loaded commercial Cu/Al₂O₃ catalysts at ambient H₂ pressure, and the optimum reaction conditions were also studied for the production of propylene.

2. Experimental

2.1. Samples

Glycerol was purchased from Wako Pure Chemical Industries, Japan. Glycerol was used for the catalytic reaction without further purification. Two types of CuO/Al₂O₃ catalysts, N242 and T317, were purchased from Nikki Chemical Co., Ltd. and Nissan Girdler Co., respectively. The weight percentage of CuO in N242 and T317 is 55.1 and 14.9%, respectively [21]. The specific surface areas of N242 and T317 are 118 and 166 m² g⁻¹, respectively [21]. SiO₂-Al₂O₃ (N631L) was purchased from Nikki Chemical. The specific surface of N631L is 440 m² g⁻¹ and the Al₂O₃ content in N631L is ca. 15 wt%. The precursors of the acidic substances such as (NH₄)₁₀W₁₂O₄₁·5H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, NH₄VO₃, Cr(NO₃)₃·9H₂O and (NH₄)₂HPO₄ were purchased from Wako Pure Chemical Industries.

Supported catalysts were prepared by an incipient-wetness impregnation method. As an example, an acid precursor of 0.586 g (NH₄)₁₀W₁₂O₄₁·5H₂O was dissolved in 15 cm³ of 30% hydrogen peroxide water for preparing a 9.3 wt% WO₃-loaded T317 catalyst. The solution with an amount of ca. 0.3 cm³ was dropped onto 5.088 g T317 catalyst for once, and the water was evaporated at an ambient pressure and 70 °C by being illuminated by a 350-W electric light bulb. After impregnation, the obtained solid was dried at 110 °C for 24 h, and then calcined at a prescribed temperature for 3 h. Hereafter, the catalysts are expressed as x%A/B, where x indicates the weight percentage of A; A indicates the species of the loaded acidic substance, and B indicates the support material. For example, 9.3%WO₃/T317 indicates 9.3 wt% WO₃ loaded on a T317 catalyst.

2.2. Catalytic reaction

The catalytic reaction of glycerol was performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at an ambient H₂ pressure. Prior to the reaction, 1.0 g of a catalyst placed in the catalyst bed was reduced at 250 °C for 1 h in an H₂ flow of 60 cm³ min⁻¹. After that, 20 wt% aqueous glycerol solution was fed through the top of the reactor at a liquid feed rate of 1.32 cm³ h⁻¹ together with H₂. The liquid effluent collected in a dry ice-acetone trap (−78 °C) every hour was analyzed by a FID-GC (GC-2014, Shi-

madzu) with a 30-m capillary column of TC-WAX (GL-Science, Japan). The gaseous products were identified by on-line gas chromatography (GC-8A, Shimadzu, Japan) with a 6-m packed column (VZ-7, GL Science, Japan). A GC-MS (QP5050A, Shimadzu) was used for identification of the products in the effluent. The conversion and selectivity were calculated as follows:

$$\text{conversion(\%)} = \frac{\text{sum of moles of all products}}{\text{sum of the reactant}} \times 100$$

$$\text{selectivity(\%)} = \frac{\text{moles of carbon in specific products}}{\text{moles of carbon in all products}} \times 100$$

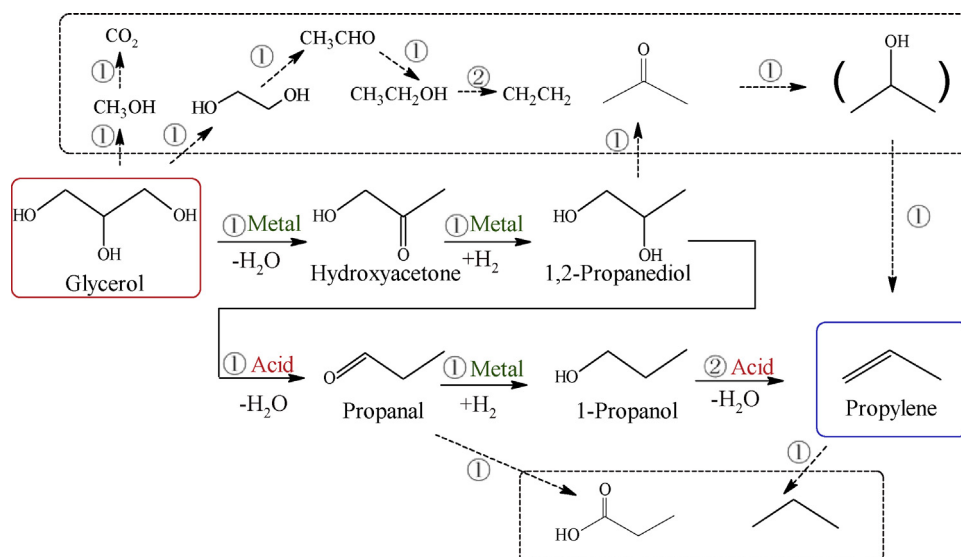
2.3. Characterization of catalysts

Temperature-programmed desorption (TPD) of adsorbed NH₃ was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution of H₂SO₄ to estimate acidity of the catalysts, as has been described in the TPD experiment of adsorbed NH₃ [48]. X-ray diffraction (XRD) patterns of the samples were recorded on a D8 ADVANCE (Bruker, Japan) using Cu Kα radiation. Temperature-programmed reduction (TPR) measurements were performed for characterizing metal state of the catalysts in a mixed flow of H₂/N₂(=1/9) at a flow rate of 10 cm³ min⁻¹ from 25 to 900 °C at a heating rate of 5 °C min⁻¹, and the details are described elsewhere [21,51].

3. Results

3.1. Hydrogenolysis of glycerol over Cu/Al₂O₃

Table 1 shows the reaction results of glycerol hydrogenolysis over two commercial Cu/Al₂O₃, T317 and N242, at different reaction temperatures. 20 wt% glycerol aqueous solution was fed into the reactor with an H₂ flow of 60 cm³ min⁻¹. At a low temperature of 190 °C over the catalysts, HA and 1,2-PDO were the main products, and the conversion of glycerol increased with increasing the reaction temperature. In the reactions of glycerol over T317, the selectivity to HA and 1,2-PDO decreased with increasing the reaction temperature, whereas the selectivity to 1-PO and propylene increased. Since 1-PO can be readily converted to form propylene by dehydration, the total selectivity to 1-PO and propylene is also summarized in Table 1. The total selectivity to 1-PO and propylene increased from 0 to 50.4% over T317 when the reaction temperature increased from 190 to 250 °C. However, in the reactions of glycerol over N242, HA and 1,2-PDO were still the main products even at 250 °C, and the total selectivity to 1-PO and propylene was only 1.3%. Acetone, PA, propionic acid, methanol, acetaldehyde, ethanol, ethylene glycol (EG), ethylene, propane, and CO₂ were also detected in the reactions, and the selectivity to the main by-products is summarized in Table 1. Scheme 1 also depicts a probable reaction route



Scheme 1. Reaction route of glycerol conversion into propylene. A product in the parenthesis is not detected during the reaction.

Table 2
Conversion of glycerol over various metal oxide-loaded T317 catalysts.^a

Catalyst	Conv. ^b (%)	Selectivity (%) ^b										
		Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
As-received T317	100	4.1	2	0.7	3.2	10.7	6.1	1.7	22.6	27.8	1	50.4
9.3%WO ₃ /T317	100	5.6	2.8	0.7	2	2.1	0.9	3.9	35.6	35.1	0.7	70.7
6.3%H ₃ PO ₄ /T317	100	2.5	2	0.9	1.3	8.2	4	1.2	24.7	29.3	2.3	54
7.3%MoO ₃ /T317	99.8	3.3	1.2	0.2	8.1	7.7	2.5	3.9	22.8	38.7	0.7	61.5
4.4%V ₂ O ₅ /T317	100	4.3	2.4	1.9	10.3	14.5	5.6	1.1	12.5	25	0.4	37.5

^a Reaction conditions: reaction temperature, 250 °C; catalyst weight, 1 g; H₂ flow rate, 60 cm³ min⁻¹; feed rate of glycerol solution, 1.32 cm³ h⁻¹. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h. Abbreviations are the same as those in Table 1.

to the products, where 2-propanol and was not detected during the reactions.

3.2. Conversion of glycerol over acid-loaded T317 catalysts

Table 2 shows the reaction results of glycerol conversion over various acid-loaded T317 catalysts. The appropriate loading of each acidic substance was determined through the individual activity tests, which catalysts with different oxide loadings were checked (the results not shown, except WO₃ in Table 3). WO₃-, H₃PO₄-, and MoO₃-loaded T317 catalysts increased the selectivity to 1-PO and propylene with decreasing the selectivity to HA and 1,2-PDO in comparison to those of the as-received T317. 6.3%H₃PO₄/T317 gave only a slight increase on the selectivity to 1-PO and propylene. The total selectivity to 1-PO increased to 61.5% over 7.3%MoO₃/T317,

whereas a slight decrease on the conversion of glycerol was observed. Among the composite catalysts, 9.3%WO₃/T317 showed the highest total selectivity to 1-PO and propylene of 70.7% and the lowest selectivity to HA and 1,2-PDO. The highest selectivity to acetone of 10.3% was observed over 4.4%V₂O₅/T317, and the total selectivity to 1-PO and propylene was lower than that of the as-received T317 without doping. In addition, the highest selectivity to acetone was 27.5% over 8.7%V₂O₅/T317.

Table 3 summarizes the reaction results of glycerol conversion over WO₃-loaded T317 catalysts at different WO₃ loadings. The selectivity to propylene increased with increasing the loading of WO₃, whereas 9.3%WO₃/T317 exhibited the highest total selectivity to 1-PO and propylene. When the loading of WO₃ increased from 9.3% to 12.3%, the conversion of glycerol slightly decreased from 100% to 99.4%.

Table 3
Conversion of glycerol over WO₃-loaded T317 catalysts at various WO₃ loadings.^a

WO ₃ content (wt%)	Acidity m mol g ⁻¹	Conv. ^b (%)	Selectivity (%) ^b									
			Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	(1-PO + propylene)
0(T317)	230	100	4.1	2	0.7	3.2	10.7	6.1	1.7	22.6	27.8	1
3.1	302	100	5.7	2.7	0.8	5.1	5.8	3.7	2.8	29.3	27.9	0.6
6.2	459	100	5.5	2.7	0.9	3	3.7	2.3	3	33.1	33.5	0.7
9.3	709	100	5.6	2.8	0.7	2	2.1	0.9	3.9	35.6	35.1	0.7
12.3	549	99.4	4.9	2.4	1	1.8	7.2	1.9	3.9	27.2	41.2	0.8

^a Reaction conditions: reaction temperature, 250 °C; catalyst weight, 1 g; H₂ flow rate, 60 cm³ min⁻¹; feed rate of glycerol solution, 1.32 cm³ h⁻¹. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h. Abbreviations are the same as those in Table 1.

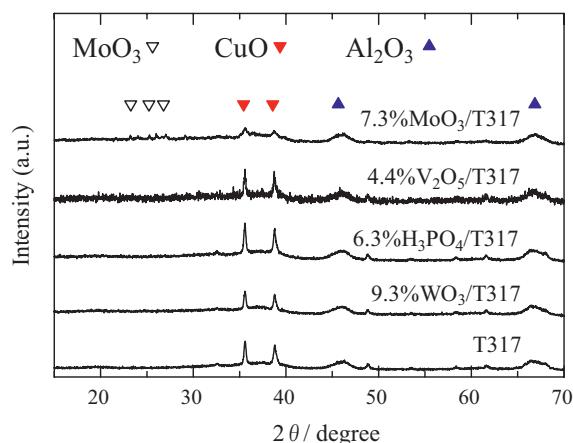


Fig. 1. XRD profiles of various acid-loaded T317 catalysts.

3.3. Characterization of acid-loaded T317 catalysts

Fig. 1 shows the XRD patterns of various acid-loaded T317 catalysts calcined at 320 °C. T317 showed the typical diffraction peaks of CuO at $2\theta = 35.5$ (–1 1 1) and 38.7° (1 1 1) [JCPDS file 5-0661] and γ -Al₂O₃ at $2\theta = 45.9$ (400) and 67.1° (440) [JCPDS file 10-425]. Diffraction peaks of MoO₃ was detected at $2\theta = 23.4$ (1 1 0), 25.7 (040) and 27.4° (02 1) [JCPDS file 5-0508] in the diffraction pattern of 7.3%MoO₃/T317. No peak attributed to H₃PO₄, V₂O₅ and WO₃ was detected in the diffraction patterns of 6.3% H₃PO₄/T317, 4.4%V₂O₅/T317 and 9.3%WO₃/T317, respectively.

Fig. 2 shows the TPR profiles of T317 and 9.3%WO₃/T317. The reduction peaks of T317 were observed at 198 and 224 °C, and the reduction peaks of 9.3%WO₃/T317 were observed at 214 and 244 °C. A broad reduction peak of 9.3%WO₃/T317 was also observed at temperatures higher than 700 °C, and it would be attributed from the reduction of WO₃ [52]. The results indicate that a temperature of 250 °C is enough for the reduction of the Cu precursors.

Fig. 3 shows the NH₃-TPD profiles of various acid-loaded T317 catalysts. T317 showed a desorption peak at 198 °C. The addition of acidic substances into T317 significantly increased the number of acid sites and also affected the acid strength. The desorption peaks of 9.3%WO₃/T317, 7.3%MoO₃/T317, 6.3%H₃PO₄/T317 and 4.4%V₂O₅/T317 were observed at 212, 185, 200 and 207 °C, respectively. Fig. 4 shows the NH₃-TPD profiles of WO₃-loaded T317 catalysts at different WO₃ loadings. The number of acid sites increased with increasing the loading of WO₃ when WO₃ loading was lower than 9.3%, and the maximum number of acid sites was recorded at a WO₃ loading of 9.3%. The desorption peaks of 3.1%WO₃/T317, 6.2%WO₃/T317, 9.3%WO₃/T317, and 12.3%WO₃/T317 were observed at 238, 225, 212 and 196 °C, respec-

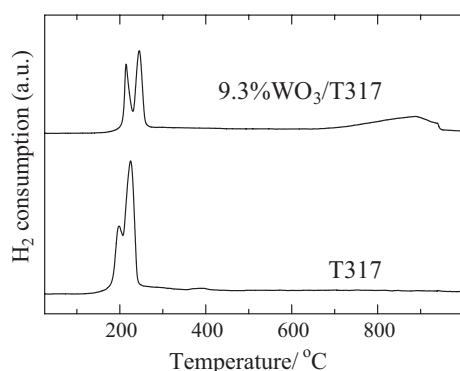


Fig. 2. TPR profiles of T317 and 9.3%WO₃/T317.

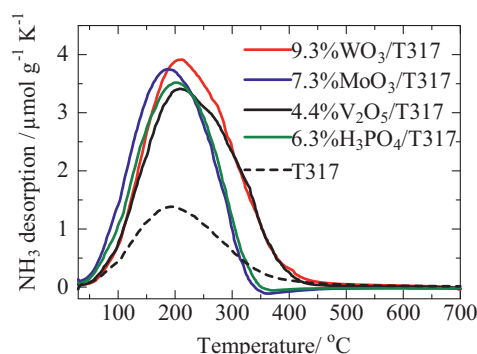


Fig. 3. NH₃-TPD of various acid-loaded T317 catalysts.

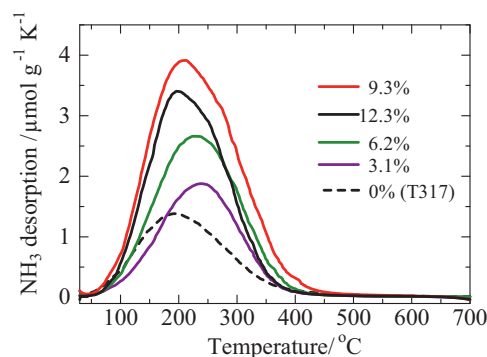


Fig. 4. NH₃-TPD of WO₃-loaded T317 catalysts at different WO₃ loadings.

tively. Table 3 summarizes the acidity of WO₃/T317 with different WO₃ loadings, which is calculated by the number of NH₃ desorbed from the acid sites. Fig. 5 shows NH₃-TPD profiles of 9.3%WO₃/T317 at different calcination temperatures. The number of acid sites decreased with increasing the calcination temperatures at calcination temperature higher than 320 °C. The desorption peaks of 9.3%WO₃/T317 calcined at 200, 320, 450 and 600 °C were observed at 283, 212, 219 and 298 °C, respectively. Table 4 also summarizes the acidity of WO₃/T317 calcined at different temperatures.

3.4. Conversion of glycerol over 9.3%WO₃/T317 at different reaction conditions

Table 4 shows the reaction results of glycerol conversion over 9.3%WO₃/T317 calcined at different temperatures. The reactions were performed at 250 °C at a H₂ flow rate of 60 cm³ min^{−1}. The total selectivity to 1-PO and propylene was low as 50.9% at a calcination temperature of 200 °C. The selectivity to 1-PO and propylene decreased, whereas the selectivity to HA and PA increased with increasing the calcination temperature at calcination temperatures

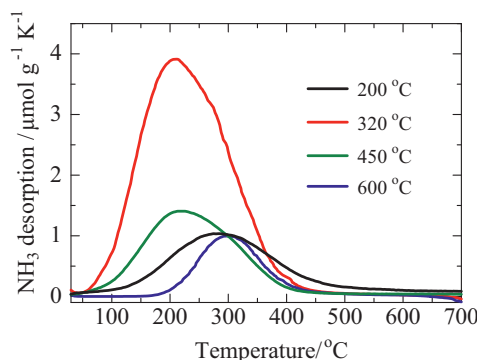


Fig. 5. NH₃-TPD of 9.3%WO₃/T317 at different calcination temperatures.

Table 4Conversion of glycerol over 9.3%WO₃/T317 catalyst at different calcination temperatures.^a

Calcination Temp. (°C)	Acidity m mol g ⁻¹	Conv. ^b (%)	Selectivity (%) ^b										
			Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
200	264	100.0	6.0	1.6	1.5	3.2	15.5	4.5	4.5	25.9	25.0	1.2	50.9
320	709	100.0	5.6	2.8	0.7	2.0	2.1	0.9	3.9	35.6	35.1	0.7	70.7
450	253	100.0	4.8	1.5	0.6	1.8	3.1	1.0	7.0	31.9	34.8	0.7	66.7
600	137	100.0	4.7	1.5	1.2	1.3	8.1	0.9	7.1	24.9	34.2	0.9	57.2

^a Reaction conditions: reaction temperature, 250 °C; catalyst weight, 1 g; H₂ flow rate, 60 cm³ min⁻¹; feed rate of glycerol solution, 1.32 cm³ h⁻¹. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h. Abbreviations are the same as those in Table 1.

Table 5Hydrogenation of glycerol over 9.3%WO₃/T317 at different H₂ flow rates.^a

H ₂ flow rate (cm ³ min ⁻¹)	Conv. ^b (%)	Selectivity (%) ^b										
		Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
30	100	6.2	2.4	0.7	3.1	7.6	0.8	4.8	31	27.8	1.2	58.8
60	100	5.6	2.8	0.7	2	2.1	0.9	3.9	35.6	35.1	0.7	70.7
120	100	4.4	3.5	0.1	1.6	0.7	0	1.8	37.4	43.4	2.1	80.7
180	100	3.8	3.5	0	1	0.2	0	1.1	38.2	47.4	1.3	85.6
180 ^c	100	3	3.1	0	0.8	0	0	1.2	31.7	50.2	3.3	81.9
240	100	3.1	2.8	0	0.8	0.3	0	0.8	28.1	57.8	1.9	85.9

^a Reaction conditions: reaction temperature, 250 °C; catalyst weight, 1 g; calcination temperature of the catalyst, 320 °C; feed rate of glycerol solution, 1.32 cm³ h⁻¹. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h.

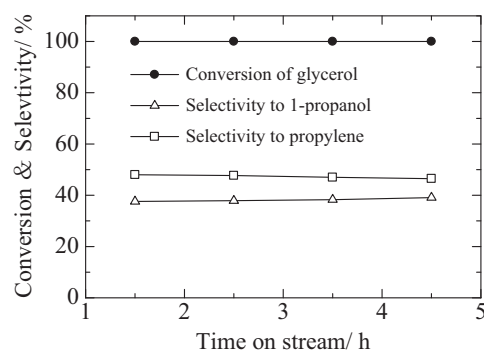
^c 4 g of catalyst was used. Abbreviations are the same as those in Table 1.

higher than 320 °C. Thus, the maximum total selectivity to 1-PO and propylene, which exceeded 70%, was achieved at a low calcination temperature of 320 °C.

Table 5 summarizes the effect of the H₂ flow rate. The reactions were performed at 250 °C at a catalyst weight of 1 g. The selectivity to 1-PO and propylene increased with increasing the H₂ flow rate up to 180 cm³ min⁻¹, whereas the selectivity to HA, 1,2-PDO, PA, EG, acetone, and methanol decreased. The total selectivity to 1-PO and propylene slightly increased from 85.6 to 85.9% when the H₂ flow rate increased from 180 to 240 cm³ min⁻¹. Since no significant change on the total selectivity to 1-PO and propylene was observed when the flow rate of H₂ increases from 180 to 240 cm³ min⁻¹ (Table 5), the effects of the reaction temperature (Table 6) and the concentration of glycerol (Table 7) were studied at a H₂ flow rate of 180 cm³ min⁻¹.

Table 6 shows the reaction results of glycerol conversion over 9.3%WO₃/T317 at different reaction temperatures. The selectivity to methanol, ethanol and propylene increased with increasing the reaction temperature. The maximum total selectivity to 1-PO and propylene was achieved at 250 °C. Fig. 6 shows the changes of the conversion and the selectivity to 1-PO and propylene with time on stream at 250 °C. The conversion of glycerol was stable at 100%, the selectivity to 1-propanol slightly increased and the selectivity to propylene slightly decreased with time on stream.

Table 7 summarizes the hydrogenation of glycerol over 9.3%WO₃/T317 at different glycerol concentrations. The selectivity

**Fig. 6.** Changes of conversion and selectivity over 9.3%WO₃/T317.

(Reaction conditions: catalyst weight, 1 g; reaction temperature, 250 °C; feed rate, 1.32 cm³ h⁻¹; H₂ flow rate, 180 cm³ min⁻¹; calcination temperature of the catalysts, 320 °C; concentration of glycerol in aqueous solution, 20 wt%)

to 1-PO and propylene decreased with increasing the concentration of glycerol in its aqueous solution, whereas the selectivity to HA, 1,2-PDO, PA, and EG increased.

3.5. Conversion of glycerol over double-bed catalysts

In Table 5, when the amount of 9.3%WO₃/T317 catalyst increased from 1 to 4 g, the selectivity to 1-PO decreased from

Table 6Hydrogenation of glycerol over 9.3%WO₃/T317 at different reaction temperatures.^a

Temperature (°C)	Conv. ^b (%)	Selectivity (%) ^b										
		Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
235	100	3	1.5	1.8	0.9	8.5	4	1.2	31.9	40.8	1.7	72.7
242	100	3.4	1.9	0.7	1.1	4	0.7	1	35	46.4	1.7	81.4
250	100	3.8	3.5	0	1	0.2	0	1.1	38.2	47.4	1.3	85.6
265	100	4.5	4.1	0	0.7	0	0	1	32.3	52.3	1	84.6
280	100	8.1	5.1	0	1.2	0	0	1.6	17.7	55.1	2.8	72.8

^a Reaction conditions: catalyst weight, 1 g; calcination temperature of the catalyst, 320 °C; H₂ flow rate, 180 cm³ min⁻¹; feed rate of glycerol solution, 1.32 cm³ h⁻¹. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h. Abbreviations are the same as those in Table 1.

Table 7
Hydrogenation of glycerol over 9.3%WO₃/T317 at different glycerol concentrations of aqueous solution.^a

Concentration (wt%)	Conv. ^b (%)	Selectivity (%) ^b										
		Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
20	100	3.8	3.5	0	1	0.2	0	1.1	38.2	47.4	1.3	85.6
40	100	5.8	2.5	0.9	2.8	3.2	0.9	3.8	39.1	31.4	1.1	70.5
60	98.1	3.8	0.5	3.3	1.4	19.1	7.5	10.1	11.4	24.6	0.6	36

^a Reaction conditions: reaction temperature, 250 °C; feed rate, 1.32 cm³ h⁻¹; H₂ flow rate, 180 cm³ min⁻¹; catalyst weight, 1 g; calcination temperature of the catalysts, 320 °C.

^b Average value in 2–5 h. Abbreviations are the same as those in Table 1.

38.2 to 31.7% and the selectivity to propylene increased from 47.4 to 50.2%. This indicates that acidic species can convert 1-PO to propylene. It is expected that acidic catalyst located under the 9.3%WO₃/T317 catalyst bed could effectively increase the selectivity to propylene. Thus, the catalytic reactions were performed at 250 °C and an H₂ flow rate of 180 cm³ min⁻¹ over double catalyst beds, in which 9.3%WO₃/T317 and a commercial silica–alumina (N631L) were charged in the upper and the lower beds, respectively.

Table 8 shows the reaction results of glycerol conversion over double-bed catalysts. A propylene selectivity of 79.1% was obtained in the double-bed catalysts, in which the catalyst charging of 9.3%WO₃/T317 and N631L was each 1 g. The reactions were also performed at different charges of N631L. The selectivity to 1-PO decreased with increasing the catalyst weight of N631L, while the selectivity to propylene increased. The selectivity to 1-PO decreased to 0%, and the propylene selectivity achieved 83.4% at an N631L charge of 3 g. Fig. 7 shows the changes in the conversion and the selectivity at an N631L charge of 3 g at 250 °C. The conversion of glycerol was stable at 100% and the selectivity to propylene slightly decreased with time on stream during 24 h. In contrast, at a lower temperature of 242 °C, an average propylene selectivity of 84.8% was obtained because of the reduction of the decomposition products such as methanol and ethanol (Table 8).

4. Discussion

4.1. Effect of the acidic substance in Cu/Al₂O₃ catalyst in the glycerol conversion into propylene

In our previous paper, N242 and T317 are found to be effective for glycerol hydrogenolysis into HA and 1,2-PDO [21]. Over N242, a high 1,2-PDO yield of 96.9% is achieved at a gradient temperature from 200 to 120 °C [21]. The present data of N242 in

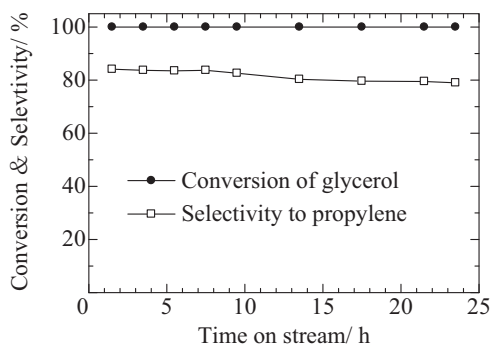


Fig. 7. Changes of conversion and selectivity over double-bed catalysts. (Reaction conditions: weight of 9.3%WO₃/T317 in the upper bed, 1 g; weight of N631L in the lower bed, 3 g; reaction temperature, 250 °C; feed rate, 1.32 cm³ h⁻¹; H₂ flow rate, 180 cm³ min⁻¹; calcination temperature of the catalysts, 320 °C; concentration of glycerol in aqueous solution, 20 wt%).

Table 1 is consistent with the results reported in a pioneering work: it can reproduce the results in Fig. 1 of Ref. [22]. Since propylene is the further hydrogenolysis product of HA and 1,2-PDO, we selected N242 and T317 as the base hydrogenolysis catalysts. In the glycerol hydrogenolysis over N242 and T317 at different reaction temperatures (Table 1), the selectivity to 1-PO and propylene increases with increasing the reaction temperature over T317 with high Al₂O₃ content. Since 1,2-PDO dehydrogenates to HA over Cu metal [16], Al₂O₃, as an acid catalyst, must promote the further conversion of 1,2-PDO to form 1-PO and propylene together with Cu metal. The total selectivity to 1-PO and propylene is only 1.3% over N242 at 250 °C, which must contribute to the small amount of Al₂O₃. Because even a weak acidic catalyst of Al₂O₃ can promote the further conversion of 1,2-PDO to form 1-PO and propylene, it is proposed that even higher selectivity to 1-PO and propylene can be achieved by the modification of T317 with proper acidic substances.

Supported WO₃, MoO₃, V₂O₅, and H₃PO₄ catalysts are well known as the acid catalysts for many kinds of reactions [53–56]. For example, ZrO₂-supported WO₃ catalyst and active carbon-supported H₃PO₄ are effective for the dehydration of glycerol to form acrolein [53,54]; γ-Al₂O₃-supported V₂O₅ and MoO₃ are effective for the selective oxidation of methanol to form dimethoxymethane and methyl formate [55,56]. In our recent paper, amorphous WO₃ supported on silica is prepared for the dehydration of 1,2-PDO into PA [49]. The supported WO₃ catalyst has a large number of acid sites and is active when prepared at a low calcination temperature of 320 °C, and a high PA yield of 93.5% is achieved at 250 °C. Since acidic substances are necessary for propylene formation in the 5-step path way from glycerol (Scheme 1), WO₃, MoO₃, V₂O₅, and H₃PO₄ were selected as the acidic substances for preparing the acid-metal composite catalysts.

The number of acid sites in the acid-loaded T317 catalysts is much larger than that of the as-received T317 (Fig. 3). Thus, it is found that all the additions of the acidic substances can increase the number of acid sites. Although WO₃-, MoO₃-, V₂O₅-, and H₃PO₄-loaded T317 catalysts show the similar NH₃-TPD profiles, the reaction results are much different. The acidic substances such as WO₃, MoO₃, and H₃PO₄ added to T317 increase the total selectivity to 1-PO and propylene. Among the composite catalysts, 9.3%WO₃/T317 shows the best performance for 1-PO and propylene formation, and the total selectivity to 1-PO and propylene increased to 70.7%. V₂O₅, however, enhances the formation of acetone. A large amount of acetone is produced in the reaction over 4.4%V₂O₅/T317 (Table 2). The hydrogenation of acetone hardly proceeds because of the low equilibrium constant [21]. Thus, it is proposed that the formation of 1-PO and propylene is not only affected by the number of acid sites and the acid strength, but also affected by the acidic properties, such as the amount of Brønsted and Lewis acid sites. How the acidic properties affect the reactions will be investigated in a further study. Although 2-propanol is not detected in the effluents collected during the reactions, it is described in Scheme 1. Even if 2-propanol is produced in the reaction, it could readily dehydrate into propylene.

Table 8
Conversion of glycerol over double-bed catalysts.^a

N631L (g)	Conv. ^b (%)	Selectivity (%) ^b										
		Methanol	Ethanol	EG	Acetone	HA	1,2-PDO	PA	1-PO	Propylene	Propane	(1-PO + propylene)
1	100	4.4	1.8	0	2	0.3	0.1	1.7	4.3	79.1	0.1	83.4
2	100	3.9	1.1	0	1.3	0.1	0	1	1	82.8	0.7	83.8
3	100	3.4	0.4	0	0.9	0	0	0.3	0	83.4	0	83.4
3.0 ^c	100	2.6	0.2	0	1	0	0	0.3	0	84.8	0.4	84.8

^a Reaction conditions: reaction temperature, 250 °C; feed rate, 1.32 cm³ h⁻¹; H₂ flow rate, 180 cm³ min⁻¹; 1.0 g of 9.3%WO₃/T317 calcined at 320 °C was charged in the upper bed and N631L was charged in the lower bed. An aqueous solution of glycerol at a concentration of 20 wt% was used as the reactant.

^b Average value in 2–5 h. Abbreviations are the same as those in Table 1.

^c Reaction temperature, 242 °C.

4.2. Effect of WO₃ loading and the calcination temperature

In the effect of WO₃ loading (Table 3 and Fig 4), the total selectivity to 1-PO and propylene is roughly proportional to the number of acid sites in WO₃-loaded T317 catalysts which is because that WO₃ can promote the conversion of 1,2-PDO to the further dehydration products. 9.3%WO₃/T317 shows the largest number of acid sites and gives the highest total selectivity to 1-PO and propylene. This clearly indicates that the additive WO₃ promotes the dehydration processes such as the routes from 1,2-PDO to PA and from 1-PO to propylene. 12.3%WO₃/T317 shows a smaller number of acid sites than that of 9.3%WO₃/T317, which possibly contributes to the agglomeration of WO₃ at a large loading because a large loading of WO₃ would decrease the catalyst surface area. In the TPR profiles (Fig. 4), the reduction temperature of 9.3%WO₃/T317 is *ca.* 20 °C higher than that of the as-received T317, which indicates the strong interaction between WO₃ and CuO.

Because the calcination temperature of silica-supported WO₃ is an important factor in the dehydration of 1,2-PDO into PA [49], the effect of the calcination temperature is also studied. The catalyst calcined at 200 °C gives the lowest total selectivity to 1-PO and propylene, which possibly contributes to that the precursor of WO₃, (NH₄)₁₀W₁₂O₄₁·5H₂O, cannot decompose completely at 200 °C [57]. The total selectivity to 1-PO and propylene seems to be proportional to the number of acid sites in the catalysts at calcination temperatures higher than 320 °C, which decreases with increasing the calcination temperature (Table 4 and Fig 5). This result is similar to that of silica-supported WO₃ in 1,2-PDO dehydration into PA [49]: amorphous WO₃ calcined at a low temperature of 320 °C has a large number of acid sites and is more active than crystalline WO₃ calcined at high temperatures. It has to be mentioned that the property of WO₃ loaded on T317 is similar to that of WO₃ loaded on silica [49], but is much different from the property of WO₃ loaded on other supports, such as ZrO₂ and TiO₂. ZrO₂ and TiO₂-supported WO₃ catalysts are well known as solid super acids [4,53], and they are usually prepared at calcination temperatures higher than 600 °C.

4.3. Effect of reaction conditions

The flow rate of H₂ significantly affects the formation of 1-PO and propylene from 1,2-PDO (Table 5). A high H₂ flow rate results a high partial pressure of H₂, which is effective for the proceeding of hydrogenation reactions because of the equilibrium shift in the hydrogenation process [21]. In particular, high H₂ flow rate promotes the hydrogenation of HA into 1,2-PDO and PA into 1-PO in this study.

The appropriate reaction temperature for 1-PO and propylene formation is 250 °C (Table 6). It has been known that silica-supported WO₃ is not so active in 1,2-PDO dehydration into PA at reaction temperatures lower than 250 °C [49]. T317-supported WO₃ is also less active at reaction temperatures lower than 235 °C,

and 1,2-PDO cannot dehydrate to PA efficiently, which results the increase in the selectivity to HA and 1,2-PDO. The selectivity to the decomposition products, such as methanol and ethanol, increases with increasing the reaction temperature, which agrees with the reaction results over N242 in our previous study [21]. Thus, 250 °C is determined as the appropriate reaction temperature for 1-PO and propylene formation from glycerol.

It has been known that the selectivity to PA decreases with increasing the concentration of 1,2-PDO over silica-supported WO₃ because the produced PA is consumed to form 2-ethyl-4-methyl-1,3-dioxolane, which is a cyclic acetal of PA with 1,2-PDO [49]. The selectivity to 2-ethyl-4-methyl-1,3-dioxolane increases with increasing the concentration of 1,2-PDO in the aqueous solution at 250 °C. In the present reaction, the concentration of glycerol also affects the formation of 1-PO and propylene (Table 7). The total selectivity to 1-PO and propylene decreases at high glycerol concentration. This indicates that the individual step-wise reactions in Scheme 1 do not proceed efficiently at a high concentration, which means a high feed rate of glycerol. In Scheme 1, the reactions with Symbol 1 are catalyzed in the upper layer catalyst, and Symbol 2 is promoted in the lower bed catalyst. It is quite reasonable that the reactions do not proceed effectively at a low contact time.

4.4. Double-bed catalysts

Although a total selectivity to 1-PO and propylene achieves 85.6% over 9.3%WO₃/T317 under the appropriate reaction conditions, 38.2% of 1-PO is not converted together with the propylene selectivity of at most 47.7%. Hydrogenolysis of glycerol over 4 g of 9.3%WO₃/T317 is performed for promoting 1-PO dehydration to achieve higher propylene selectivity, whereas the change on the selectivity to 1-PO and propylene is small (entry 5 of Table 5). Thus, WO₃ loaded on T317 is effective for promoting 1,2-PDO dehydration into PA, whereas it is not so effective for promoting 1-PO dehydration into propylene. On the other hand, silica-alumina is well known as an acid catalyst for alcohol dehydration, such as 1-butanol dehydration into butenes [58]. On the contrary, glycerol is decomposed into acetaldehyde together with the formation of acrolein and 1,2-PDO at 325 °C over a silica-alumina catalyst placed in the single bed without using Cu catalyst [3].

To establish efficient direct conversion of glycerol to propylene, glycerol conversion is performed over double-bed catalysts, in which 9.3%WO₃/T317 is charged in the upper bed and a commercial silica-alumina, N631L, is charged in the lower bed to complete the conversion of 1-PO to propylene (Table 8). The selectivity to propylene increases to 79.1% and the selectivity to 1-PO decreases to 4.3% when 1 g of N631L is used in the lower bed. This demonstrates that the double-bed catalyst system is effective for the direct formation of propylene from glycerol via multi steps. Even higher propylene selectivity can be obtained by increasing the charging of N631L, which can convert 1-PO to propylene completely. A high propylene selectivity of 83.4% was achieved at an N631L charge of 3 g.

Over 250 °C, the selectivity to the decomposition products increases with increasing the reaction temperature (Table 6). Since HA and 1,2-PDO cannot be converted further at a temperature lower than 235 °C (Table 6), we selected a reaction at 242 °C to maximize the selectivity to propylene from glycerol (entry 4 in Table 8). HA and 1,2-PDO are completely converted at a low temperature, which is favorable in the equilibrium of endothermic hydrogenation [21], and a decrease of the selectivity to the decomposition products is also observed at 242 °C. As a result, the selectivity to propylene achieved a maximum of 84.8%. It has to be mentioned that HA and 1,2-PDO were not detected over the double-bed catalysts, while those were detected over the single-bed 9.3%WO₃/T317 (Table 6). We propose that the real pressure of H₂ in double-bed catalysts system may slightly be higher than the atmospheric pressure because of the large loading of powdered catalysts. And it has been known that high pressure of H₂ is efficient for HA and 1,2-PDO hydrogenolysis into 1-PO and propylene.

Recently, Yu et al. have reported the production of propylene from glycerol with a selectivity of 88% at a conversion of 73% over double-bed catalysts of Ir/ZrO₂ and HZSM-5 at 250 °C and 0.5 MPa [50]. A high H₂ pressure increases the conversion of glycerol, whereas it decreases the selectivity to propylene because of promoting the further hydrogenation of propylene to propane. In the present process, however, both the complete conversion of glycerol and a high selectivity to propylene are obtained at ambient H₂ pressure. Because of the inexpensive Cu-based catalyst and the mild reaction conditions, an economical production of propylene from glycerol through this process can be expected.

5. Conclusions

Vapor-phase conversion of glycerol into propylene was studied over Cu/Al₂O₃ and acid-loaded Cu/Al₂O₃ catalysts at ambient H₂ pressure. Cu/Al₂O₃ with a low copper content, T317, was much more active for 1-PO and propylene formation from glycerol than that with a high copper content, N242, because T317 had a larger amount of Al₂O₃, which worked as an acid catalyst to promote 1,2-PDO dehydration into PA, than that of N242. The loading of acidic substances, such as WO₃, MoO₃ and H₃PO₄, on T317 increased the selectivity to 1-PO and propylene by promoting the dehydration of 1,2-PDO into PA. 9.3%WO₃/T317 showed the best catalytic performance among the composite catalysts. The calcination temperature significantly affected the number of acid sites in 9.3%WO₃/T317, which affected the total selectivity to 1-PO and propylene. 9.3%WO₃/T317 calcined at 320 °C showed the largest number of acid sites and gave the highest total selectivity to 1-PO and propylene. The appropriate reaction conditions are as follows: temperature, 250 °C; H₂ flow rate, 180 cm³ min⁻¹ and concentration of glycerol, 20 wt%. Furthermore, the conversion of glycerol over double-bed catalysts, in which 9.3%WO₃/T317 was charged in the upper bed and a commercial SiO₂-Al₂O₃ was charged in the lower bed, was performed to promote the conversion of 1-PO into propylene. A high propylene yield of 84.8% was obtained over the double-bed catalysts at 242 °C.

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